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## Meteorological and Chemical Factors Controlling Ozone Formation in Seoul during MAPS-Seoul 2015

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### ABSTRACT

To understand the chemical mechanisms of controlling factors in ozone (O<sub>3</sub>) formation in early summer in Seoul, a comprehensive study encompassing measurement and modeling was conducted under the Megacity Air Pollution Study-Seoul (MAPS-Seoul) campaign. From May 18 to June 12, 2015, O<sub>3</sub> and peroxyacetyl nitrate (PAN) were measured, along with their precursors, including NO<sub>x</sub> and volatile organic compounds (VOCs), at the Korea Institute of Science and Technology, located in northeast Seoul. VOCs were sampled in a canister twice a day (at 09:30 and 15:00) and analyzed via gas chromatography. The meteorological conditions and chemical regimes of the air masses were clearly distinguished during the study period. In May, NO<sub>x</sub> concentrations were higher with more pronounced diurnal cycles of precursors and O<sub>3</sub> under constant westerly winds. By contrast, stagnant conditions developed in June, which reduced the inflow of primary emissions from the downtown area but increased the influence from the neighboring forest under high temperatures. As a result, the ratio of O<sub>3</sub> to odd oxygen was higher in June, indicating a less efficient removal of O<sub>3</sub> by NO<sub>x</sub>. In the same context, the air mass was chemically more aged with a higher NO<sub>2</sub>/NO<sub>x</sub> ratio and enhanced OH reactivity of oxygenated and biogenic VOCs in June. The overall measurement results suggest that O<sub>3</sub> formation is slightly more sensitive to VOCs than to NO<sub>x</sub> in Seoul during this season, when O<sub>3</sub> concentrations are the highest of the year.

**Keywords:** O<sub>3</sub> formation; NO<sub>x</sub>; VOCs; Meteorological condition; MAPS-Seoul.

### INTRODUCTION

The exposure to high concentrations of O<sub>3</sub> has adverse effects on human health (Thurston and Ito, 2001), forest ecosystems, agriculture (Fuhrer, 2003; Karnosky *et al.*, 2005), and global climate (Hogrefe *et al.*, 2004; Hubbell *et al.*, 2005). Various plans implemented with the view of controlling O<sub>3</sub> and reducing the emission of its precursors,

including nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs), resulted in declining O<sub>3</sub> levels in the U.S. (Kleinman *et al.*, 2005; Russell *et al.*, 2012; Pollack *et al.*, 2013), Mexico City (Sillman and West, 2009), Europe (Adame Carnero *et al.*, 2010; Kaltsonoudis *et al.*, 2016), Japan (Sadanaga *et al.*, 2012), and Taiwan (Chou *et al.*, 2006), which contrasts the situation in China (Duan *et al.*, 2007; Han *et al.*, 2011; Zhu *et al.*, 2015).

In Seoul, the capital of South Korea, the O<sub>3</sub> concentration increased during the 1990s and seemed to slightly decrease in the early 2000s, when public attention rapidly turned to PM<sub>10</sub> owing to record-high values of Asian dust being recorded in 2002 (KMOE, 2016). However, recent studies have indicated that the O<sub>3</sub> level in Seoul has increased again since 2005 (Ghim and Chang, 2000; Kim *et al.*, 2005; Han *et al.*, 2013). In other major cities of Korea, the O<sub>3</sub> concentration is also increasing over time (e.g., An *et al.*,

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2015). In particular, the number of days for which the O<sub>3</sub> concentration exceeded 120 ppbv (hourly average) has greatly increased nationwide over the last decade (Choi, 2014; Seo *et al.*, 2014).

To abate O<sub>3</sub> pollution in the Seoul Metropolitan Area (SMA), a multiyear study was conducted in the eastern parts of Seoul (at Olympic Park and Korea University) during 2002–2005 (Lee *et al.*, 2008). The main results of these studies suggest that O<sub>3</sub> formation in Seoul is VOC-limited. The concentrations of total VOCs and NO was reduced in Seoul (KMOE, 2016) by a reinforced policy to limit emissions. However, NO<sub>2</sub> concentrations have not decreased proportionally, leading to a higher NO<sub>2</sub>/NO<sub>x</sub> ratio (Han *et al.*, 2013). This is consistent with the increased O<sub>3</sub> observed in most urban areas in Korea (e.g., An *et al.*, 2015). NO<sub>x</sub> reduction was likely more effective due to the use of low-emission vehicles and natural gas than to VOC emission control because of illicit emissions from small facilities (Lee *et al.*, 2015; Kim *et al.*, 2017).

The later studies also demonstrate that O<sub>3</sub> formation is generally VOC-limited in Seoul (Fu *et al.*, 2012; Jin *et al.*, 2012; Yoo *et al.*, 2015). In other megacities around the world, the ambient O<sub>3</sub> concentrations are either VOC-limited or NO<sub>x</sub>-limited, depending on the characteristic VOC/NO<sub>x</sub> ratio (Stephens *et al.*, 2008; Sadanaga *et al.*, 2012; Jing *et al.*, 2014; Zhang *et al.*, 2014b). Downwind of Shanghai, Tie *et al.* (2013) demonstrated that O<sub>3</sub> formation switched from VOC-limited to NO<sub>x</sub>-limited with a threshold ratio NO<sub>x</sub>/TVOC of 0.1–0.2, which was estimated based on a WRF-Chem model. In the Mexico City Metropolitan Area, the urban core region is VOC-limited and the surrounding rural area is mostly NO<sub>x</sub>-limited; however, this can change depending on the weather (Song *et al.*, 2010). When VOC-limited conditions often dominate, such as with heavy traffic in the large metropolitan areas of California, reduction of NO<sub>x</sub> would lead to enhanced local O<sub>3</sub> concentrations (Marr and Harley, 2002; Murphy *et al.*, 2007).

Recently, several studies have highlighted that VOC reactivity significantly affects O<sub>3</sub> production. Pusede *et al.* (2014) reported that the total organic reactivity increases exponentially with temperature during high-O<sub>3</sub> days in the San Joaquin Valley. Over the urban Houston area, the variation of O<sub>3</sub> concentration is estimated to be 5–25 ppb in conjunction with the changes in isoprene emissions by  $\pm 50\%$  (Li *et al.*, 2007). Filella and Penuelas (2006) also indicated that VOC species such as acetaldehyde, methanol, and acetone, which all have a significant biogenic component, play an important role in O<sub>3</sub> formation. Given high biogenic loading, the O<sub>3</sub> production rate is more sensitive to changes in the VOC concentration (Li *et al.*, 2007; Kim *et al.*, 2013).

This study was conducted as a part of the Megacity Air Pollution Study-Seoul (MAPS-Seoul) 2015 campaign. The main objective of MAPS-Seoul is to single out the mechanisms and factors that contribute to O<sub>3</sub> formation in early summer (May–June), when O<sub>3</sub> concentrations are the highest of the year and most frequently exceed the standard level of 100 ppbv (hourly average). This study thus thoroughly examines the temporal variations of O<sub>3</sub>, its precursors—including NO<sub>x</sub> and VOCs—and photochemical indicator species such as PAN and discusses the controlling factors and chemical mechanism of O<sub>3</sub> formation in Seoul.

## METHODS

Ambient O<sub>3</sub>, NO<sub>x</sub>, CO, VOCs, and PAN were measured at the campus of the Korea Institute of Science and Technology (KIST) (37°36′10″N, 127°2′46″E) from May 18 to June 12, 2015. The measurement site is located in the northeastern part of Seoul, which is 37 km from east to west. The inner-city highway with heavy traffic passes to the north and west of the KIST and the Hongneung Experimental Forest (35.3 ha) run by the Korea Forest Service sits to the east and south (Fig. 1).



**Fig. 1.** Map showing the measurement site of at KIST (Korea Institute of Science and Technology, 37°36′10″N, 127°2′46″E), located in northeast Seoul. The site is surrounded by an inner-city highway to its north and west (~250 m away) and the Hongneung Experimental Forest to its east and south (~150 m away).

O<sub>3</sub> was measured via ultraviolet absorption (KENTEK, Mezus410, Korea) with a detection limit of 0.1 ppbv. NO and NO<sub>2</sub> were measured using chemiluminescence with a molybdenum converter (KENTEK, Mezus210, Korea). The detection limit of NO and NO<sub>2</sub> was 50 ppt. CO was detected using a gas filter correlation technique (KENTEK, Mezus 310, Korea). The NO<sub>x</sub> and CO instruments were calibrated against zero air and span gas (400 ppbv NO and 4 ppm CO) every 3 days. Ozone monitor was calibrated before and after the field campaign using the standard reference photometer of KRISS (Korea Research Institute of Standards and Science). PAN was measured every 2 min via fast gas chromatography with luminol chemiluminescence detection. The detailed method of PAN measurement and calibration is well described in previous studies (Gaffney *et al.*, 1998; Lee *et al.*, 2008; Han *et al.*, 2017). The calibration of PAN was done by the nitration of peracetic acid in *n*-tridecane with the synthesized standards, and its nominal detection limit is 100 pptv (Lee *et al.*, 2008). All measurement instruments were installed in a container house and the height of the inlets was approximately 3 m above the ground. For data analysis, hourly averages of all these measurements were merged together.

For VOCs, whole-air samples were collected in a 2-L canister twice a day and chemical analysis was done at the University of California, Irvine (UC Irvine), after the field measurements. Canisters were preconditioned at UC Irvine and shipped to Korea University. Air samples were collected for 3 min at 09:30 and at 15:00. A total of 23 samples were acquired over 12 days, including one morning sample on June 10. The detailed methods and procedures for the canister collection are well documented elsewhere (Blake *et al.*, 2001; Blake *et al.*, 2003; Simpson *et al.*, 2010). In this study, the entire period of storage and shipping lasted no longer than one month. Any artifacts associated with the sampling were thus estimated to be less than 5 pptv (Kim *et al.*, 2016). For these canisters, 81 non-methane hydrocarbon species were analyzed via gas chromatography coupled to three flame-ionization detectors, an electron capture detector for halocarbons, and a quadrupole mass spectrometer detector for sulfur compounds. Of these, 43 species were selected for further discussion in the present study. The detailed analytical methods are described in Colman *et al.* (2001).

Meteorological parameters, including UV radiation, temperature, relative humidity, wind speed, and wind direction, were continuously measured at the KIST site. To examine how changes in air mass affected the measurement, the air-mass trajectory was traced backward using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLOT) model with a global data assimilation system (GDAS, 1 degree) from the U.S. National Oceanic and Atmospheric Administration (NOAA) (Wang, 2014). Trajectories were calculated and plotted using the Trajstat software.

## RESULTS AND DISCUSSION

### Measurement Overview

For the entire experiment period, the time-series variations of O<sub>3</sub>, PAN, NO, NO<sub>2</sub>, CO, and temperature are

presented in Fig. 2. The VOC concentrations are given for the subclasses. The temperature increased gradually from May to June and the hourly maximum temperature (34°C) was recorded on June 10. The daily maximum temperature exceeded 30°C for a total of 9 days over the entire period.

In Korea, O<sub>3</sub> concentration is generally highest during May–June, which is before the summer monsoon season. In 2015, the monthly average concentration of O<sub>3</sub> was also high in May and June in Seoul (KMOE, 2016). The high hourly mean O<sub>3</sub> concentrations of over 100 ppbv occurred 23 times in 6 days. Of these, two O<sub>3</sub>-event days occurred in May (6 times) and four in June (17 times) with the highest hourly concentration of 143 ppbv occurring on June 10. For the six O<sub>3</sub>-event days, daily mean and maximum concentrations of O<sub>3</sub> and PAN are given in Table 1 with the results of other measurements. In addition, the O<sub>3</sub> diurnal variations are presented with monthly averages in Fig. 3. These O<sub>3</sub> concentrations in Seoul are not as high as those observed in other big cities that suffer from bad air quality. In Beijing, during the summer of 2005, O<sub>3</sub> levels exceeded 120 ppbv for 13 out of 39 days of the experiment period with an hourly maximum concentration of 286 ppbv at a northern mountainous site (Wang *et al.*, 2006). In the Houston metropolitan area of the U.S., the O<sub>3</sub> concentration reached over 200 ppbv in 2000 (Banta *et al.*, 2005).

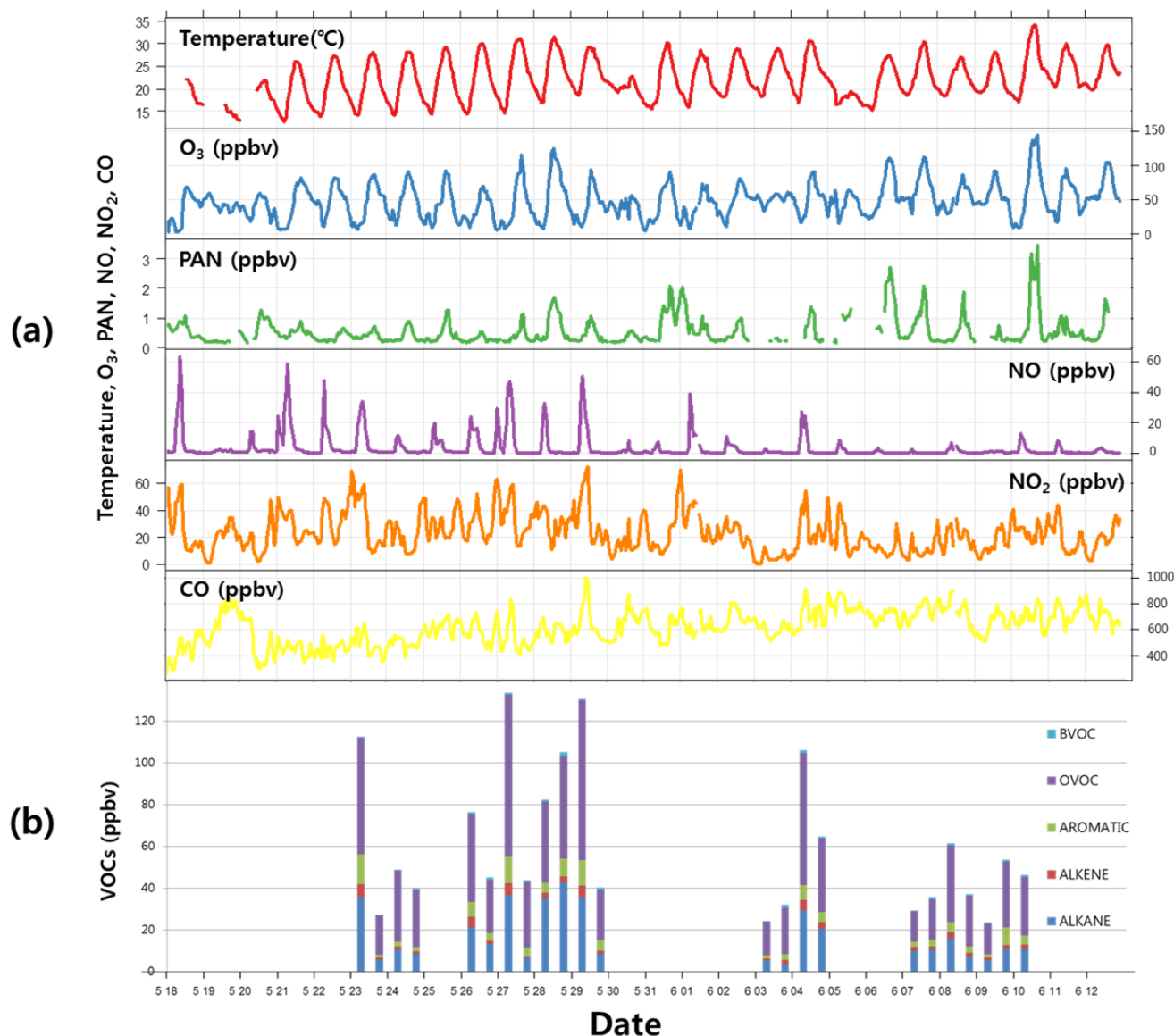
In the present study, O<sub>3</sub> concentrations show a diurnal variation typical of polluted urban sites, which are characterized by a clear maximum concentration during the day and very low concentration during the night. The amplitude of the diel cycle was approximately 60 ppbv for the entire period, with no significant difference between May and June because O<sub>3</sub> concentrations were higher in June than in May during both daytime and nighttime (Fig. 3). It is noteworthy that O<sub>3</sub> concentrations rose to approximately 40 ppbv during the night in June. The average concentration of O<sub>3</sub> was also higher in June than in May (Fig. 4). The concentration difference between May and June is noticeable and is consistent with all measured species in the present study, as discussed further below.

PAN also exhibits a typical diurnal variation similar to that of O<sub>3</sub>. The maximum concentration was 3.4 ppbv, which was observed on June 10. The mean concentration of PAN for the entire measurement period was 0.5 ppbv, which was generally comparable with the concentrations from a previous study by Lee *et al.* (2013) conducted in Seoul during June 2011 but was apparently lower than those measured during May–June in 2004–2005 (Lee *et al.*, 2008). PAN has been intensively measured in Beijing and the concentrations were much higher than the results of Seoul for similar O<sub>3</sub> concentrations (Zhang *et al.*, 2014a). The maximum PAN concentrations in Beijing exceeded 10 ppbv in May and June 2010.

The average NO<sub>x</sub> concentration was 26.7 ppbv for the entire experiment. Contrary to O<sub>3</sub>, NO<sub>x</sub> concentration was higher in May than in June (Fig. 4). In particular, a morning NO peak occurred regularly in May but was much less clear in June. Consequently, the average concentration of NO and NO<sub>2</sub> was 5.4 and 26.6 ppbv in May and 1.8 and 18.5 ppbv in June, respectively.

VOCs were measured twice a day (09:30 and 15:00 local time) for 12 days. In this study, the five subclasses of VOCs were considered as O<sub>3</sub> precursors and were included in the total VOCs (TVOCs): alkane, alkene (including

acetylene), aromatic and oxygenated VOCs (OVOCs), and biogenic VOCs (BVOCs). Of the TVOCs, OVOCs account for the largest fraction of over 50%, followed by alkane, aromatics, alkene, and BVOCs. Among the OVOCs,

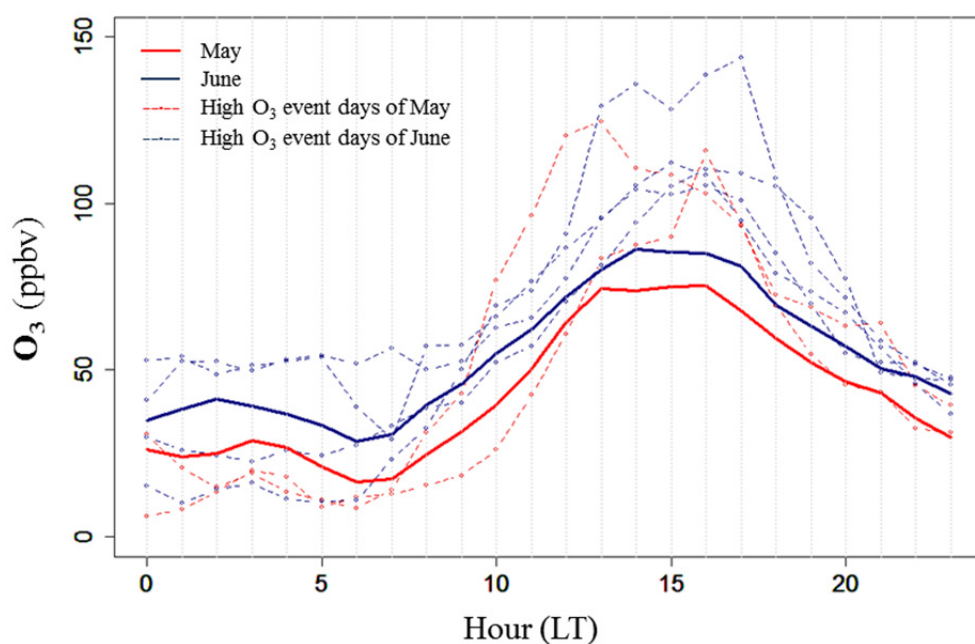


**Fig. 2.** (a) Time-series variation of measured species of 1-h-average including Temperature, O<sub>3</sub>, PAN, NO, NO<sub>2</sub>, and CO. (b) VOC concentrations (ppbv) presented as cumulative bars for five subgroups: BVOC, OVOC, aromatic, alkene, and alkane. The two bars correspond to the morning (9:30) and afternoon (15:00) samples.

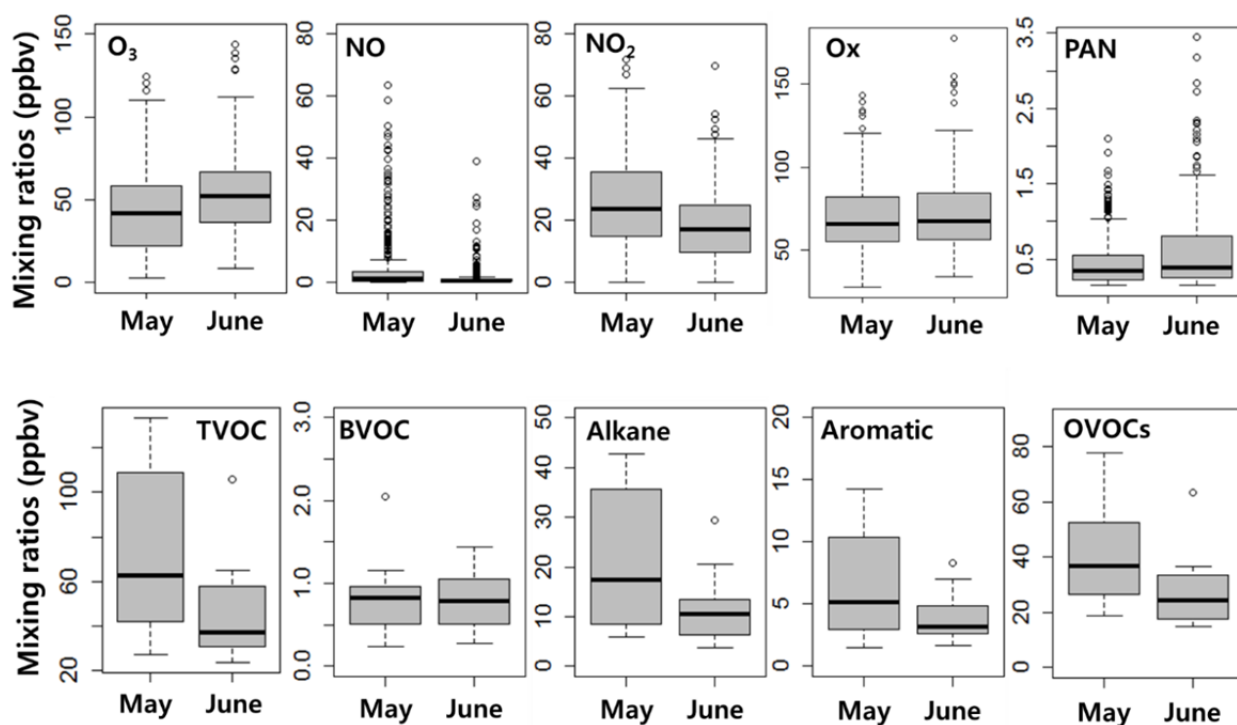
**Table 1.** Summary of measurement statistics for the O<sub>3</sub>-event days (1-h average over 100 ppbv) observed at KIST site.

Event day	O <sub>3</sub> (ppbv)		PAN (ppbv)		NO (ppbv)	NO <sub>2</sub> (ppbv)	CO (ppbv)	TVOC (ppbc)	Temperature (°C)	
Concentration	Mean	Max	Mean	Max	Mean	Mean	Mean	Mean	Mean	Max
May 27	42.0	115.8	0.37	1.14	10.8	35.0	540	258	23.4	31.1
May 28	58.0	124.6	0.69	1.68	4.5	30.9	587	282	24.2	31.7
June 6	58.0	110.3	1.36	2.73	0.7	12.7	706	NA	21.7	27.5
June 7	66.6	112.0	0.70	2.09	0.5	9.7	732	95	23.3	30.5
June 10	63.3	143.8	0.95	3.44	2.2	24.6	689	130	25.0	34.2
June 12	66.2	105.4	0.54	1.61	0.9	17.4	706	NA	23.9	29.8





**Fig. 3.** Diurnal variations of  $O_3$  for the six high- $O_3$ -event days with monthly mean variations for May and June. Daily and monthly variations are presented by dashed and solid lines, respectively, with May and June marked in red and blue, respectively.



**Fig. 4.** Concentrations (ppbv) of  $O_3$ ,  $NO$ ,  $NO_2$ ,  $O_x$  ( $O_3 + NO_2$ ),  $PAN$ , total VOCs, and their four subgroups (except alkene) are compared for May and June. Boxes and whiskers indicate the inner quartile of the 25<sup>th</sup> and 75<sup>th</sup> percentiles and 5<sup>th</sup> and 95<sup>th</sup> percentiles, respectively. The solid line in the boxes is the median. Outliers are represented as open circles.

acetone and methanol are the most abundant. For alkanes and alkenes, propane and ethene concentrations were the highest, respectively. Toluene is still the most abundant among aromatic VOCs in the present study, whereas its concentration was the highest of all VOCs in Seoul during

2004 to 2005 (Lee *et al.*, 2008). In general, VOC concentrations were higher in the morning than in the afternoon and higher in May than in June, similar to the situation for  $NO_x$ . The average TVOC concentration was 73.7 ppbv in May and 46.6 ppbv in June (Table 2).

### Meteorological Factors Controlling Precursor Concentrations

The levels of  $O_3$  and its precursors, including  $NO_x$  and VOCs, show a visible difference in concentrations between May and June. In addition to chemical species, wind pattern was found to be distinct between the two months (Fig. 5(a)). While westerly winds were dominant in May, easterly winds were frequent in June; therefore, stagnant

conditions developed in June. As the study region is under the influence of the Asian monsoon system, southerly winds from the ocean bring heavy rain in the summer from July to September and northerly winds are strong in the winter. In the SMA, June is the pre-monsoon season and is characterized by stagnant conditions with relatively low wind speeds.

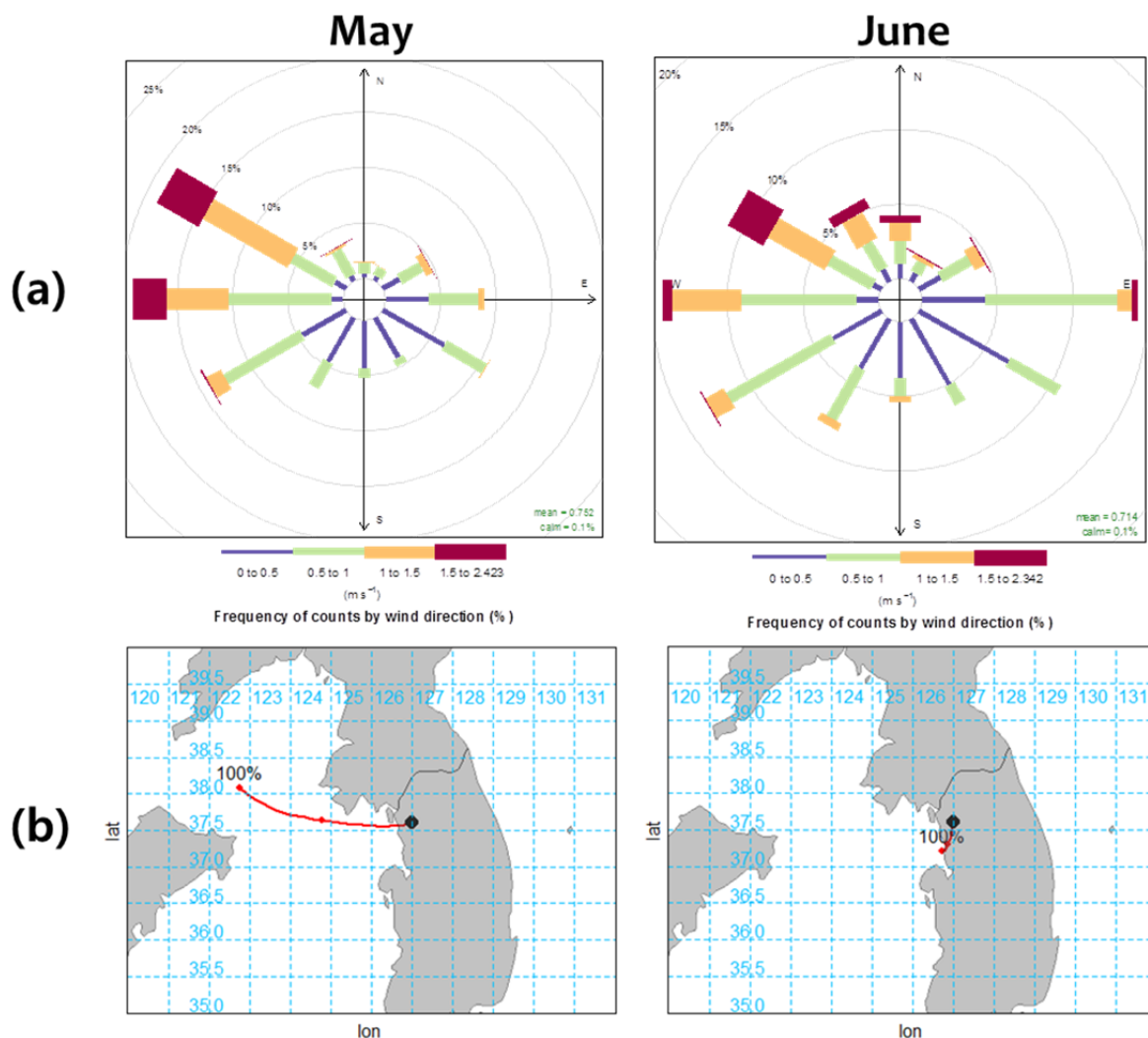
In May, westerly winds consistently brought urban

**Table 2.** The average concentrations of VOC sub-classes for all measurements.

Concentration (ppbv)	All	May		June	
		9:30 (n = 6)	15:00 (n = 6)	9:30 (n = 6)	15:00 (n = 5)
TVOC <sup>#</sup>	60.8	97.4	50.2	48.4	44.6
alkane	16.9	29.1	14.2	12.7	10.5
alkene	2.6	4.4	1.5	2.4	2.2
aromatic	5.3	8.9	4.2	3.7	4.4
OVOC	35.1	54.3	29.3	28.9	26.5
BVOC	0.8	0.6	1.0	0.6	1.0

<sup>\*</sup> n: number of samples.

<sup>#</sup> TVOC (Total VOC), OVOC (Oxygenated VOC), and BVOC (Biogenic VOC).



**Fig. 5.** (a) Wind roses for May and June. Wind speeds are given as ranges. (b) The 24-h HYSPLIT backward trajectories of air masses arriving at the site over 1000 m at 15:00 (LT) averaged for May (left) and June (right).

emissions from Seoul to the site, accumulating  $\text{NO}_x$  and VOCs to the east. In Seoul, vehicles are the main source of emissions (KMOE, 2016) and are responsible for the highest  $\text{O}_3$  concentrations observed in the eastern part of Seoul (KMOE, 2016). In contrast, there was no dominant wind in June. In addition to local winds, we compared the back trajectories of air masses over the two months. The trajectories calculated for 24 h are averaged for each month and presented in Fig. 5(b). The trajectory analysis clearly shows the difference in atmospheric conditions between May and June and the stagnation of the air mass in June. In previous studies, meteorological factors such as wind direction and speed and temperature were reported to be important factors in the distribution of pollutants in the SMA (Ghim *et al.*, 2001; Lee *et al.*, 2008). Furthermore, the present study demonstrates that, in the SMA, the levels of  $\text{NO}_x$  and VOCs were greatly affected by meteorological conditions. Large-scale stagnation, in conjunction with high temperature, has been pointed to as the main reason for high- $\text{O}_3$  episodes (Yin *et al.*, 2009). In Houston, the extreme excess of  $\text{O}_3$  seemed to be more frequent during stagnation episodes (Davis *et al.*, 1998). Hou and Wu (2016) claimed that the extreme air pollution was significantly affected by atmospheric stagnation.

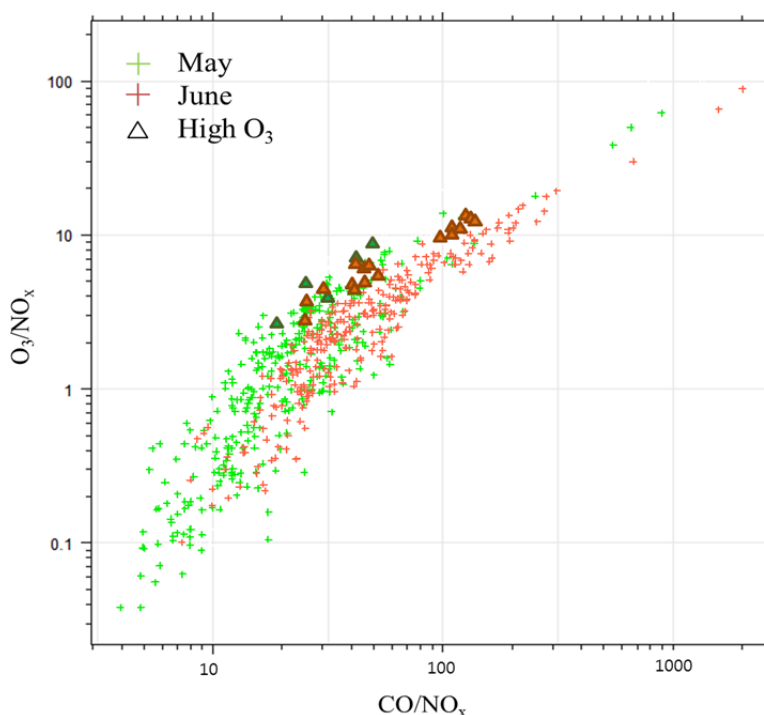
#### Photochemical Characteristics of Air Masses

If the distribution of  $\text{O}_3$  precursors is largely affected by meteorological conditions, what would be the consequence of their photochemical reactions for the characteristics of air masses? Here, we compared the ratios  $\text{O}_3/\text{NO}_x$  and

$\text{CO}/\text{NO}_x$  for all measurements based on Morgan *et al.*'s (2010) observation that these ratios increase with distance from the source upon the evolution of air masses. Thus, the higher these ratios are, the more air masses are aged. For our measurements, the ratios  $\text{O}_3/\text{NO}_x$  and  $\text{CO}/\text{NO}_x$  increased proportionally (Fig. 6). Surprisingly, the chemical characteristics of air masses were also distinguished between May and June, implying that air masses are more aged in June than in May. While the May air masses show chemical properties typical of near-urban areas, they were categorized as near source in June. In the present study, the effect of chemical evolution on air-mass aging is well captured over time, as was originally described over distance by Morgan *et al.* (2010). It is likely that while fresh emissions from the SMA were pumped into the site by constant westerlies in May, photochemical reactions exerted more influence on air masses under the stagnant conditions in June. The ratios of high- $\text{O}_3$  days fall into the near-source category, even for episodes of May. This result emphasizes that meteorological conditions can boost  $\text{O}_3$  formation by fostering photochemical processing and precursor transport.

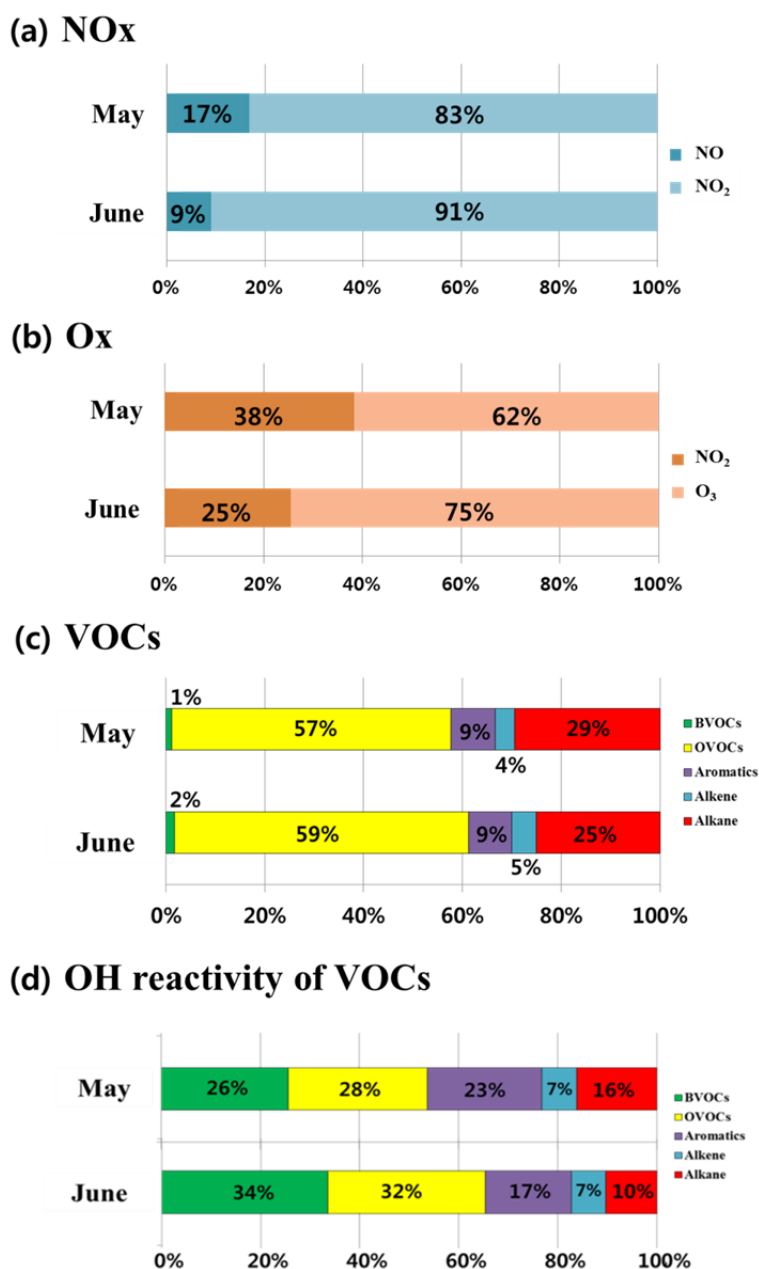
#### Characteristic Ratios of Precursors

While the mean  $\text{NO}$  and  $\text{NO}_2$  concentrations were much higher in May than in June, the  $\text{NO}_2/\text{NO}_x$  ratio was higher in June than in May (Fig. 7(a)). As indicated in Fig. 3, the nighttime  $\text{O}_3$  was higher in June than in May, which is primarily associated with  $\text{NO}_x$  levels. In urban areas under high  $\text{NO}_x$  concentration, the reaction with  $\text{NO}$  is a major process of  $\text{O}_3$  loss, where  $\text{NO}$  is rapidly converted to  $\text{NO}_2$



**Fig. 6.**  $\text{O}_3/\text{NO}_x$  ratio as a function of  $\text{CO}/\text{NO}_x$  ratio based on hourly measurements in May (green cross) and June (orange cross). The high- $\text{O}_3$ -event days are marked in black. In this plot, the chemical regime of air masses is classified as “near urban,” “near source,” and “near outflow” according to whether the ratio  $\text{O}_3/\text{NO}_x$  is  $< 1$ , between 1 and 10, or  $> 10$ , respectively (Morgan *et al.*, 2010).





**Fig. 7.** Fraction of (a) NO and NO<sub>2</sub> in NO<sub>x</sub>, (b) NO<sub>2</sub> and O<sub>3</sub> in O<sub>x</sub>, (c) BVOC, OVOC, aromatics, alkanes, and alkenes in total VOCs, and (d) their OH reactivity as a percent of total reactivity in May and June. For this comparison, monthly averages were used.

(Tang *et al.*, 2012). Thus, odd oxygen ( $O_x = O_3 + NO_2$ ) represents the actual level of O<sub>3</sub>. The level of O<sub>x</sub> was higher mainly because of higher O<sub>3</sub> concentration in June than in May (Fig. 4), leading to a 13% increase in the O<sub>3</sub>/O<sub>x</sub> ratio in June (Fig. 7(b)). This is clear evidence that the NO<sub>x</sub>-O<sub>3</sub> reaction effect is substantial in determining O<sub>3</sub> concentrations in Seoul.

In addition, the higher NO<sub>2</sub>/NO<sub>x</sub> ratio indicates a rapid recycling of NO to NO<sub>2</sub> by HO<sub>2</sub> and RO<sub>2</sub> radicals. Although the concentrations of VOCs were higher in May than in June (Fig. 4), the relative abundance of subclasses did not significantly differ between the two months (Fig. 7(c)). When converting the VOC concentration to OH reactivity,

the relative contribution of each VOC subclass demonstrated a clear difference (Fig. 7(d)). While the relative contributions to OH reactivity from the most abundant VOCs, including OVOCs and alkane, decreased, the contributions from BVOCs and aromatics increased notably in June. Considering a low concentration of BVOCs no higher than 1%–2% of the TVOCs, BVOCs were the most powerful source of odd hydrogen, accounting for 34% of the total OH reactivity of VOCs in June. These results suggest that BVOCs played a significant role in O<sub>3</sub> formation, particularly during the late afternoon in June when air was stagnant. Note that the forest is just to the east of the site, so its influence would be greater under stagnant conditions.

BVOCs were already recognized as an important, if not dominant,  $O_3$  precursor in rural and urban areas (Chameides *et al.*, 1988; Khattatov *et al.*, 1999; Calfapietra *et al.*, 2013; Kim *et al.*, 2013; Zou *et al.*, 2015). The findings of the present study suggest that BVOC emissions need to be considered in developing a policy to control  $O_3$  concentration, even in greater Seoul.

The relative ratio of VOCs to  $NO_x$  is a critical factor for policy making for future  $O_3$  control. TVOCs-to- $NO_x$  ratios greater than 15 are often considered  $NO_x$ -limited and ratios less than 4 are considered VOC-limited (NRC, 1991). In the present study, these ratios were less than 8 (Fig. 8). Thus, the relation between TVOCs and  $NO_x$  suggests that  $O_3$  formation in the SMA falls into the VOC-sensitive regime.

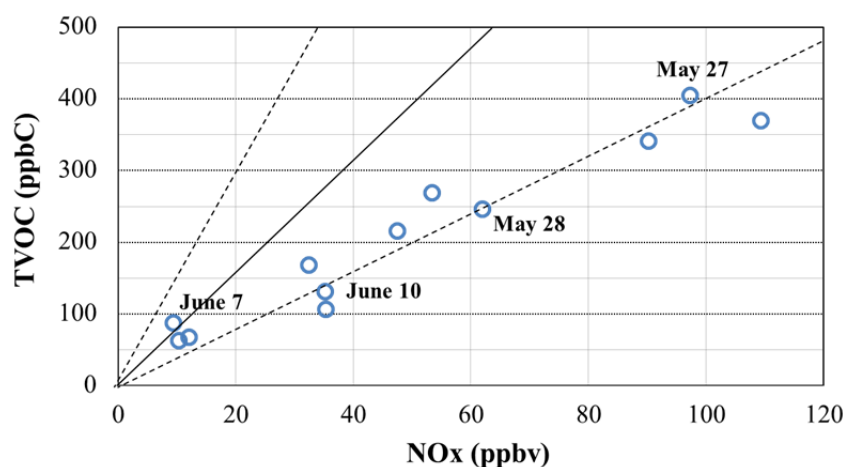
### Effect of Temperature on $O_3$ Formation

As typical of most urban areas, the daily maximum  $O_3$  concentrations are related to the daily maximum temperature with the highest  $O_3$  found on the warmest days. Previous studies demonstrated a positive correlation between  $O_3$  concentration and temperature (Cox and Chu, 1996; Tagaris *et al.*, 2007; Lee *et al.*, 2008; Pusede *et al.*, 2015). In the present study, the daily maximum temperature of hourly mean over  $30^\circ\text{C}$  occurred four times in May and five times in June, and the high- $O_3$  episodes of hourly mean concentrations over 100 ppbv occurred on May 27 and 28 and June 6, 7, 10, and 12 (Table 1), for which there is a fairly good correlation ( $R = 0.87$ ) between daily maximum temperature and  $O_3$  concentration (Fig. 9(a)). For all hourly measurements,  $O_3$  concentrations correlated well with temperature ( $R = 0.78$ ) (Fig. 9(b)). The slope of  $4.43 \text{ ppbv } ^\circ\text{C}^{-1}$  is greater than what was observed in rural sites of the eastern U.S. during ozone season for 22 years (Bloomer *et al.*, 2009). They reported that the sensitivity of  $O_3$  to temperature was decreased in accordance with reduction in  $NO_x$  by 43%. In this study for two months of high- $O_3$  period in Seoul, however, the sensitivity of  $O_3$  to temperature was greater in June ( $5.04 \text{ ppbv } ^\circ\text{C}^{-1}$ ) under lower  $NO_x$  (20 ppbv) than in May ( $3.68 \text{ ppbv } ^\circ\text{C}^{-1}$ ) under higher  $NO_x$  (31 ppbv).

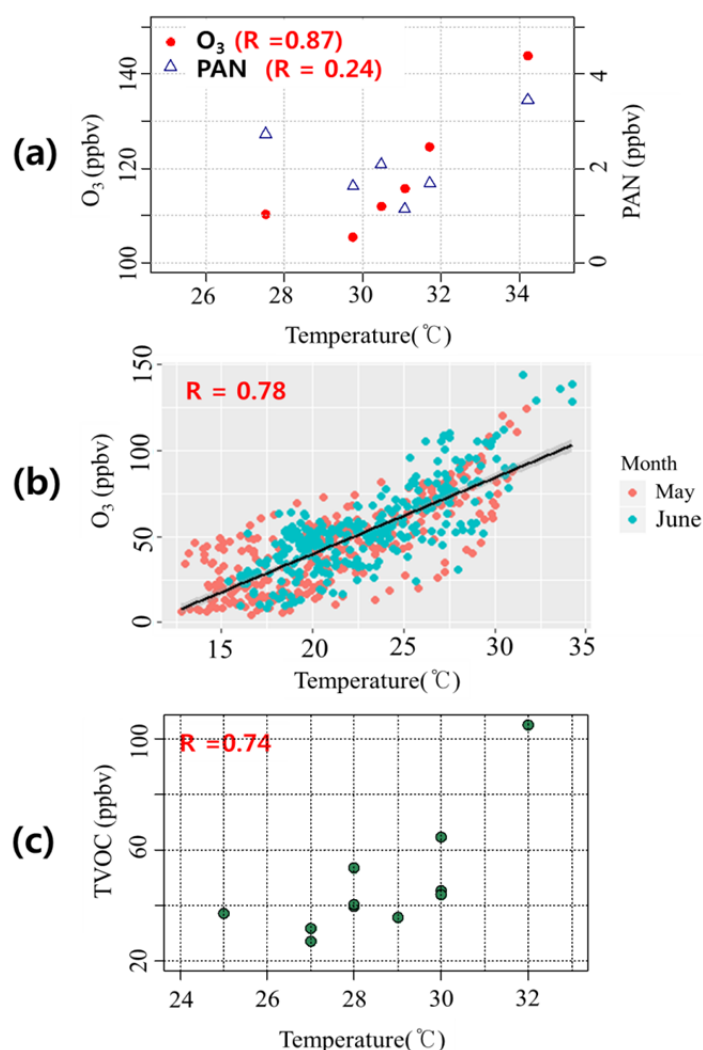
Indeed, it demonstrates that the  $O_3$  formation of Seoul was limited by VOCs. Unlike  $O_3$ , the temperature dependence was unclear for PAN, which is not consistent with what was observed in Seoul approximately 10 years ago (Lee *et al.*, 2008). It is also noteworthy that TVOC concentrations increased linearly with temperature (Fig. 9(c)). For these, the main causes should be elucidated through further studies. Considering global warming and expectations for the future, the correlation of chemical species with temperature could be crucial in developing policies to abate air pollution.

### CONCLUSION

Measurements of  $O_3$ ,  $NO_x$ , CO, PAN, and VOCs were conducted as part of the Megacity Air Pollution Study-Seoul (MAPS-Seoul) campaign on the campus of the Korea Institute of Science and Technology in Seoul from May 18 to June 12, 2015. During the experiment, the mean hourly  $O_3$  concentration exceeded the national standard of 100 ppbv by 23 times over six days, with the highest concentration, 143 ppbv, occurring on June 10. The  $O_3$  exceedances occurred more frequently in June (17 times over four days) than in May (6 times over two days). In contrast to  $O_3$ , the  $NO_x$  and VOC concentrations were higher in May than in June, with mean concentrations of 31.2 and 73.7 ppbv in May and 20.5 and 46.6 ppbv in June, respectively. The monthly difference in precursor distribution primarily resulted from meteorological conditions. Whereas constant westerly winds brought primary emissions from downtown Seoul to the measurement site in May, the air mass became stagnant in June. In the study region, June is a transition period for air masses from the Asian continent to the Pacific Ocean, causing stagnant conditions to develop just before the monsoons. As a result, the concentrations of  $NO_x$  and alkanes, which were mainly emitted from vehicles, were considerably higher in May than in June. Backward trajectories of the air masses also confirm the difference in atmospheric conditions.



**Fig. 8.** The morning concentrations of total VOC (TVOC) and  $NO_x$  are correlated. VOCs were sampled at 9 a.m. and  $NO_x$  is hourly mean concentration for 8–9 a.m. Four high- $O_3$ -event days are marked as dates on the plot. The lines denote the TVOC/ $NO_x$  ratio of 15, 8, and 4.



**Fig. 9.** (a) Correlation between daily maximum temperature and daily maximum  $O_3$  and PAN concentration for the six high- $O_3$ -event days, (b) correlation between the hourly  $O_3$  concentrations and temperature for the entire measurement, and (c) correlation between total VOC concentration (ppbv) and temperature at 15:00.

Under low  $NO_x$  conditions in June, the odd-oxygen concentration was comparable to that observed in May. As a result, the ratio of  $O_3$  to odd-oxygen increased by 13% in June, indicating that the  $NO_x$ - $O_3$  reaction plays a crucial role in determining  $O_3$  concentration. The average diurnal variations of the two months demonstrate that the difference in  $O_3$  concentrations was greater during nighttime than daytime. In addition, the ratio of  $NO_2/NO_x$  was higher in June than in May, implying a more efficient recycling of NO into  $NO_2$  by  $HO_2$  and  $RO_2$  radicals. While VOC concentrations differed between the two months, the VOC compositions were similar in relative abundance. In the present study, oxygenated VOCs and ethane are the most abundant among the five VOC subclasses. Although the abundance of BVOCs was no higher than 2% on average, its contribution to the OH reactivity was notably increased, being comparable to and even higher than that of OVOCs in May and June, respectively. It is highly likely that the relative contribution of BVOCs from the neighboring forest was greater in June, when stagnant conditions developed.

In the present study, the daily maximum concentration of  $O_3$  correlated well with the daily maximum temperature, which is consistent with the results of previous studies. In addition, the correlation was fairly good for all measurements of the hourly concentrations. It is also noteworthy that the total VOC concentration increased with the temperature. These results emphasize that temperature is a key factor controlling  $O_3$  concentrations through its effect on precursor concentrations and through photochemical mechanisms. Although precursor levels have decreased over the last couple of decades, the formation of  $O_3$  remains more sensitive to VOCs than to  $NO_x$  in Seoul, particularly during the pre-monsoon season of summer.

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